

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

0 343 247
A1

(12)

EUROPEAN PATENT APPLICATION
published in accordance with Art.
158(3) EPC

(21) Application number: 88906883.9

(51) Int. Cl. 4: **B01D 13/01** , **B01D 13/04** ,
C08J 9/26 , **D01F 6/12**

(22) Date of filing: 28.07.88

(96) International application number:
PCT/JP88/00755

(87) International publication number:
WO 89/00879 (09.02.89 89/04)

(30) Priority: **30.07.87 JP 193322/87**
30.07.87 JP 193323/87
13.11.87 JP 287627/87

(43) Date of publication of application:
29.11.89 Bulletin 89/48

(84) Designated Contracting States:
AT BE CH DE FR GB IT LI LU NL SE

(71) Applicant: **TORAY INDUSTRIES, INC.**
2-1, Nihonbashi Muromachi 2-chome
Chuo-ku
Tokyo 103(JP)

(72) Inventor: **KAWAI, Takashi**
B2-23, 10, Sonoyama 2-chome Otsu-shi
Shiga 520(JP)
Inventor: **KATSU, Tomoko**
Wakakusa Ryo 1-1, Ohe 1-chome
Otsu-shi Shiga 520(JP)
Inventor: **YOSHIOKA, Toshio**
1-44, Ichiriyama 2-chome Otsu-shi
Shiga 520(JP)

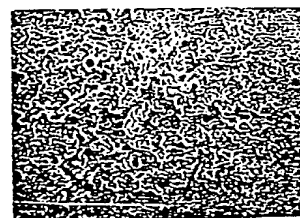
(74) Representative: **Coleiro, Raymond et al**
MEWBURN ELLIS & CO. 2/3 Cursitor Street
London EC4A 1BQ(GB)

(54) **POROUS POLYMETRAFLUOROETHYLENE MEMBRANE, SEPARATING APPARATUS USING SAME, AND PROCESS FOR THEIR PRODUCTION.**

EP 0 343 247 A1

(57) This invention is related to a porous hollow filament membrane mainly composed of a polytetrafluoroethylene resin and a process for producing a porous membrane, which comprises forming a mixture of a polytetrafluoroethylene resin dispersion with a filament-forming polymer into a hollow or sheet-like form, heat-treating the resulting membrane at a temperature above the melting point of the resin, and removing the filament-forming polymer. This process enables porous polytetrafluoroethylene resin membranes with various pore sizes and void ratios to be produced by changing the kind or

amount of additives to the starting mixture, and provides a new technique of separating substances in a high-temperature and strongly decomposing or strongly dissolving medium.



Xerox Copy Centre

POLYTETRAFLUOROETHYLENE RESIN POROUS MEMBRANE, SEPARATOR MAKING USE OF THE POROUS MEMBRANE AND METHODS OF PRODUCING THE POROUS MEMBRANE AND THE SEPARATOR

Technical Field

The present invention relates to a novel polytetrafluoroethylene resin porous membrane suitable for use in condensation and separation of substances by, for example, ultrafiltration, fine filtration and so forth, as well as to a separator making use of this porous membrane and methods of producing the porous membrane and the separator.

Background Art

Hitherto, porous membranes of cellulose acetates, polyethylenes, polypropylenes, polymethacrylates, polyacrylonitriles and polysulfonates have been used in processes such as reverse osmosis, ultrafiltration, fine filtration and so forth. Unfortunately, however, these known porous membranes are still unsatisfactory because of heat-resistance and chemical-resistance properties, in particular anti-alkali, anti-acid and anti-solvent properties.

Under this circumstance, studies have been made on production of porous membranes from polytetrafluoroethylene (referred to as "PTFE" hereinafter). For instance, specifications of the United States Patent Nos. 3,953,566 and 4,096,227 disclose methods in which a non-sintered PTFE resin blend containing a liquid lubricant is extruded at a high temperature and the extruded material is drawn and heated to about 327°C or above, whereby a polytetrafluoroethylene resin porous membrane is formed. These methods, however, suffer from inferior performance of the product due to small controllability of the porous structure or inferior membrane-formability which results in an impractically large thickness of the product membrane.

Accordingly, an object of the present invention is to provide a PTFE resin porous membrane which is free from the above-described problems of the prior art, as well as a separator which makes use of this porous membrane and which exhibits superior heat- and chemical-resistance properties with an extremely small rate of elution.

Disclosure of the Invention

The present invention provides a porous hollow

fiber membrane made mainly from a polytetrafluoroethylene resin.

The present invention also provides a method of producing a porous membrane comprising: forming a membrane having a hollow construction or a sheet-like construction from a mixture of a polytetrafluoroethylene resin dispersion and a fiber-forming polymer; heat-treating the membrane at a temperature not lower than the melting point of the resin; and removing the fiber-forming polymer.

The present invention further provides a membrane-type separator comprising: a separator case; a porous membrane made mainly from a polytetrafluoroethylene resin; and a sealing material with which an end of the separator case is sealed, the sealing material containing a fluoro-resin.

The present invention further provides a method of producing a separator comprising: forming a membrane having a hollow construction or a sheet-like construction from a mixture of a polytetrafluoroethylene resin dispersion and a fiber-forming polymer; heat-treating the membrane at a temperature not lower than the melting point of the resin; and effecting the following steps (1) and (2) in combination on the heat-treated film:

(1) removing the fiber-forming polymer, and

(2) mounting the membrane in a case so as to form independent flow channels in the case and welding and fixing an end of the case with a fluoro-resin.

Best Mode for Carrying Out the Invention

The present invention will be described in more detail hereinafter.

The PTFE resin used in the invention is a tetrafluoroethylene homopolymer or a copolymer which contains not less than 50 mol%, preferably not less than 60 mol% and more preferably not less than 80 mol% of tetrafluoroethylene in terms of monomer unit, e.g., a tetrafluoroethylene-perfluoroalkylvinyl copolymer, a tetrafluoroethylene-hexafluoropropylene copolymer, a tetrafluoroethylene-ethylene copolymer and so forth, or their mixture.

In the production processes according to the invention, the PTFE resin material is used in the form of an aqueous dispersion or an organic solvent dispersion, preferably in the form of an aqueous dispersion formed by an emulsification polymerization in an aqueous medium containing a

surfactant or a liquid formed by condensing such an aqueous dispersion. More specifically, the dispersion contains PTFE resin particles of a particle size not greater than 1μ , preferably not greater than 0.8μ , uniformly dispersed therein.

The fiber-forming polymer used in the present invention generally covers all polymers which are capable of forming fibers and which are capable of providing a formable mixture when mixed with the PTFE resin dispersion. When an aqueous dispersion liquid is used, a viscose polymer (cellulose sodium xanthate polymer), a polyvinylalcohol polymer or a sodium alginate polymer is preferably used as the fiber-forming polymer, independently or in the form of a mixture thereof.

The mixing ratio of the fiber-forming polymer to the PTFE resin varies depending on the type of the fiber-forming polymer used in the invention. The above-mentioned mixing ratio, however, preferably ranges between 10 and 200 wt%, more preferably between 30 and 100 wt%. Porous membranes having mean pore size of 0.01μ or greater cannot be obtained when the mixing ratio of the fiber-forming polymer is less than 10 wt%. On the other hand, a mixing ratio exceeding 200 wt% reduces the mechanical strength of the formed membrane to an impractically low level.

According to the present invention, it is preferred to add an additive or additives for the purpose of improving porosity and formability when the PTFE resin dispersion and the fiber-forming polymer are mixed with each other.

Any additive which can be removed by heat-decomposition, extraction, dissolution or radioactive decomposition may be used as the above-mentioned additive. For instance, one or more of the following additives are suitably used: a silicate such as calcium silicate or aluminum silicate; a carbonate such as calcium carbonate or magnesium carbonate; a phosphate such as sodium phosphate or calcium phosphate; an acetate; an oxalate; a chloride such as ammonium chloride; a sulfate such as sodium sulfate or barium sulfate; a nitrate; a weak or strong acid salt such as a perchlorate; a powdered metal such as iron powder; a metal oxide such as alumina, zirconia or magnesium oxide; a pulverized organic matter such as pulverized silicate, kaolin clay and diatomaceous earth; a pulverized resin such as of polyamide, polyester, polyolefin, polysulfone, polyvinyl chloride, polyvinylidene fluoride or polyvinyl fluoride; and a heat-resistant organic matter such as silicone oil, hexafluoropropylene oxide oligomer, chlorotrifluoroethylene oligomer, phthalic acid ester, trimellitic acid ester, sebacic acid ester, adipic acid ester, azelaic acid ester or phosphoric acid ester.

It is also possible to add a commercially available surfactant or a de-foaming agent for the pur-

pose of improving the stability of the membrane-forming mixture and improving membrane formability, as well as fiber-formability.

The total amount of the additive or additives used in the present invention varies depending on factors such as the types of the additive or additives, types of the PTFE resin and the types of the fiber-forming polymer. In general, however, the total amount of the additive or additives is preferably 1000 wt% or less of the PTFE resin, because the mechanical strength of the product membrane is impractically lowered when the additive or additives are added in excess of 1000 wt%.

No appreciable effect in the control of the porous structure cannot be produced when the amount of the additive or additives is below 10 wt%.

Thus, the amount of the additive or additives preferably ranges between 30 and 700 wt%, more preferably between 50 and 500 wt%.

The mixing of the PTFE resin dispersion liquid and the fiber-forming polymer is conducted at a temperature which is preferably not higher than 100°C , because mixing at temperatures above 100°C causes aggregation of the resin particles in the dispersion liquid and the additive or additives which are used as desired, resulting in a clogging of a filter during formation or in lack of uniformity of the structure of the formed material. The mixing temperature, therefore, is 80°C or less, preferably 60°C or less and more preferably 40°C or less.

According to the invention, the uniform mixture is subjected to a forming process which is executed by rolling, extrusion or a combination thereof. The uniform mixture is prepared in the form of a liquid which exhibits a viscosity level of 10 to 10000 poise, preferably 100 to 5000 poise, at the forming temperature.

The concentration of the PTFE resin in the uniform mixture varies depending on factors such as the types of the fiber-forming polymer and additive as used, forming method and so on. In general, however, the PTFE resin concentration ranges between 1 and 50 wt%, preferably 5 and 30 wt%.

The formed material in the present invention can have the form of a sheet, a tube or a hollow fiber, among which the hollow fiber is most preferred because it provides a large effective area per unit volume and because it permits the size of the apparatus and the production cost to be reduced advantageously.

For instance, the formed material is formed by spreading a formable mixture on the surface of a flat plate such as a sheet of a glass or a metal or on the surface of a continuous belt and then coagulating the spread material by dipping the same in a coagulating liquid. The formed material also may

be formed by extruding a formable mixture through a slit into a coagulating liquid directly or indirectly through the air. A method also is usable in which a formable mixture is extruded together with a core of a non-coagulative or coagulative fluid from a spinneret for spinning a hollow fiber into a coagulating liquid directly or indirectly through the air so as to coagulate the formable mixture. Alternatively, a formable material is extruded together with a core of a coagulating liquid into a non-coagulative fluid directly or indirectly through the air, thereby coagulating the formable mixture.

The type of the non-coagulative fluid cannot be definitely determined because it depends on the type of the fiber-forming polymer. Generally, however, the non-coagulative fluid is suitably selected from substances such as water, glycerol, ethylene glycol, polyethylene glycol, liquid paraffin, isopropylmyristate, freon and their mixtures, as well as from gases such as air, nitrogen, and inert gases.

Spinneret temperature also depends on the viscosity of the material liquid and, hence, cannot be definitely determined, though it generally ranges between 20 and 120°C. It is also preferred that the spinneret is maintained at or above a temperature which is 20°C below the coagulating liquid temperature. Such a spinneret temperature is effective in preventing deterioration in the spinning characteristics attributable to condensation of vapor on the spinneret surface which is serious particularly when the distance between the spinneret surface and the coagulation liquid surface is small.

When the extruded formable mixture is introduced into the coagulating liquid indirectly via the air, it is preferred from the view point of forming stability that the distance traveled by the mixture from the spinneret surface to the coagulation liquid surface ranges between 0.2 and 200 cm. In this case, the temperature of the air is the same as the ambient air temperature or the room temperature. In some cases, however, the air may be cooled to a lower temperature.

The type of the coagulating liquid varies depending on the type of the fiber-forming polymer as used. In general, however, the following substances are usable as the coagulating liquid independently or in the form of a mixture: an aqueous solution of an inorganic salt such as sodium sulfate, ammonium sulfate, zinc sulfate, potassium sulfate, calcium sulfate, copper sulfate, magnesium sulfate, aluminum sulfate, calcium sulfate, magnesium chloride, zinc chloride or the like; and an acid such as sulfuric acid, hydrochloric acid, nitric acid, acetic acid, oxalic acid, boric acid or the like. The temperature of the coagulating liquid is a factor which significantly affects the formability and is generally selected to range between 0 and 98°C.

The heat-treatment in the present invention can be executed at the melting point of the PTFE resin or higher temperature in various types of atmosphere such as vacuum, air, nitrogen, oxygen, sulfur gas, helium gas or silicone oil. The heat-treatment may be conducted with or without tension applied to the material, either in a batch mode or a continuous mode. Various methods are adoptable such as a method in which the material is treated in a free state without being fixed, a method in which the material is drawn and fixed to a treating frame in advance of the heat-treatment, and a method in which the treatment is conducted while fixing the material on a treating frame with a given length or a shrinkage, or a method in which these methods are suitably combined to treat the material continuously.

The drawing may be effected before, after or during the heat-treatment. A too large drawing factor or ratio causes the pores to be undesirably elongated in the drawing direction or the pore size becomes uncontrollable with the result that the product membrane becomes unreliable in terms of the permeability. From this point of view, the drawing factor or ratio is determined to range between 1.1 and 3. The drawing temperature also is selectable within the range between the room temperature and the heat-treating temperature. The drawing may be conducted not only uni-axially but also bi-axially.

One of the critical features of the present invention resides in that the fiber-forming polymer is removed from the formed material after the heat-treatment. The fiber-forming polymer, however, may have changed its nature as a result of the heat-treatment.

The removal of the fiber-forming polymer or the additive from the formed material after the heat-treatment may be effected by a suitable method such as dissolution, decomposition or a combination thereof, by means of a liquid, gas, heat or radioactive rays. The removal may be conducted in a batch-mode or in a continuous mode. Alternatively, the removal may be effected after installation of the formed material in a module or an element.

Various removing methods are usable depending on the types of the fiber-forming polymer and the additive. In general, however, a method can conveniently be used in which the formed material after the heat-treatment is dipped in a liquid which is composed mainly of an acid such as sulfuric acid, nitric acid, hydrochloric acid, perchloric acid or fluoric acid alone or in the form of a mixture thereof or an alkali such as sodium hydroxide or potassium hydroxide alone or in the form of a mixture thereof. Alternatively, this liquid is circulated through a module or an element loaded with the formed material.

The removal of the fiber-forming polymer conducted after installing the formed material in a module or an element encounter a difficulty in the removal of the polymer in the regions where the formed material is fixed by welding, often resulting in presence of a trace amount of residual polymer. Therefore, where there is a strict demand for elimination of eluate, it is advisable that the fiber-forming polymer is removed from the edge portions of the heat-treated material before the fixing of the same by welding to the module or the element.

It is also possible to subject the thus formed membrane to a drawing so as to improve properties such as the permeability, mechanical strength and dimensional stability. The drawing factor or ratio is about 1.1 to 3, while the drawing temperature usually ranges between the room temperature and the melting point of the PTFE resin.

The membrane of the present invention can be used in a dry state. However, according to the present invention, since the PTFE resin is hydrophobic, it is necessary that the membrane is subjected to a treatment for rendering the fine pores hydrophilic. In such a case, the membrane may be stored in the wetted state after the treatment. The wetness can be maintained by allowing deposition of various wetting agent such as water-containing glycerol, ethylene glycol, polyethylene glycol, various surfactants, and so forth.

The porous membrane according to the present invention preferably has no substantial orientation of the shapes of pores when viewed on a plane parallel to the membrane surface. More specifically, the ratio of the maximum value of the mean pore size as measured unidirectionally to the mean pore size as measured in the orthogonal direction is not greater than 5, preferably not greater than 3.

The membrane can have a composite construction composed of a fine structure layer and a support layer. The size and number of the pores in the fine structure layer, as well as the thickness of the same, are important factors which significantly affect the water permeability and solute blocking ratio of the membrane.

The membrane of the invention with the composite structure may have at least one fine structure layer on the surface of the membrane. In such a case, the membrane thickness which rules the permeation speed is reduced as compared with the case where the membrane is formed of the fine structure layer alone. In this case, a sharp dividing characteristic with a high permeability is obtained by supplying a liquid to be treated from the same side as the fine structure layer. In addition, it is possible to remove any gel layer formed on the surface of the fine structure layer, by applying a pressure to the reverse side of the membrane, thus

proving a superior backwash characteristic. In addition, there is no risk for the delamination of the fine structure layer from the support layer, because the fine structure layer has been formed on the surface of the support membrane simultaneously with the formation of the support layer.

The support layer has a multiplicity of pores having a mean pore size greater than 2μ , preferably between 2 and 20μ , as measured in a plane parallel to the membrane surface. In addition, the support layer is formed integrally and continuously with the fine structure layer and serves to bear mechanical load applied thereto. The pores of the support layer need not always be arranged isotropically. The pores of the support layer may have forms elongated in the thicknesswise direction of the membrane with their longitudinal axes having lengths not smaller than 20μ . Preferably, however, the pores are shaped without any substantial orientation when viewed in a plane parallel to the membrane surface. More specifically, the ratio of the maximum value of the mean pore sizes measured uni-directionally to the mean pore size measured in the orthogonal direction is not greater than 5, preferably not greater than 3.

It is also preferred that the porosity of the membrane of the present invention is not smaller than 20%.

Any resin having a melting point which is not higher than the melting point of the resin as the porous membrane material can be used as a bonding resin for fixing the edges of the porous membrane. Thus, a fluoro-resin, an olefin resin, an imide resin, an acrylonitrile resin, an amide resin or an ester resin can suitably be used as the bonding resin.

When an extremely small rate of eluate and specifically high heat- and chemical-resistances are required, the following fluoro-resins are preferably used as the bonding resin, as well as the PTFE resin having a melting point of about 327°C : tetrafluoroethylene-perfluoroalkylvinyl copolymer resin (melting point 306°C); tetrafluoroethylene-hexafluoropropylene copolymer resin (melting point about 260°C); vinylidene fluoride polymer resin (melting point about 174°C); chlorotrifluoroethylene polymer resin (melting point about 211°C). More preferably used are a combination of a PTFE resin porous membrane (melting point about 327°C) and the same resin, a combination of the PTFE resin porous membrane and a tetrafluoroethylene-perfluoroalkylvinyl copolymer resin (melting point about 306°C), and a combination of the PTFE resin porous membrane and a tetrafluoroethylene-hexafluoropropylene copolymer resin (melting point about 270°C), as well as a combination of a porous membrane of tetrafluoroethylene-perfluoroalkylvinyl copolymer resin (melting point about

270°C) and a tetrafluoroethylene-hexafluoropropylene copolymer resin (melting point about 270°C). The bonding resin may be used in various forms such as pellets, powder, sheet, dispersion and so forth.

The method of the present invention for producing a separator comprises: (1) removing the fiber-forming polymer from the formed material after a heat-treatment; and (2) fixing by welding, edges of the formed material by means of a PTFE resin. The removal of the fiber-forming resin may be executed in advance of the fixing or, alternatively, after the fixing.

The nature of the fiber-forming polymer may have been changed from the initial state, as a result of the heat-treatment.

The formed material after the heat-treatment contains fiber-forming polymer filling fine pores so as to produce a reinforcement effect. Therefore, no substantial change is caused in the shape and the porous structure of the formed material even when the formed material is heated to a temperature above the melting point of the PTFE resin. This effect can be enjoyed when the method of the invention is carried out such that the removal of the fiber-forming polymer is conducted after the fixing of the formed material.

There is no restriction in the fixing of the formed material by welding. For instance, the heating for welding may be effected only on local portions of the edge of the formed material or over the entire length of the edge to be welded. The welding heat can be applied by various means such as a heating iron, a heater of various type, an oven, a supersonic bonder, and so forth. In order to achieve a high sealing effect at the weld region, it is preferred that the welding is conducted under an increased or decreased pressure or, alternatively, under application of vibration or centrifugal force.

When the formed material has a pipe-like form, tubular form or a hollow fiber form, the following measures are preferably taken in order to prevent deformation or collapse of the formed material. For instance, a suitable reinforcer such as a rod, wire, filament or fiber of a metal, glass or a ceramic is inserted into the internal hollow or cavity of the formed material. Alternatively, a resin filler or an adhesive which cannot be molten at the heating temperature is charged into desired portion of the hollows or cavities. After the production of a module by welding, the bar or the filler is removed by pulling, chemical decomposition or extraction.

In a preferred form of the method of the invention for producing a separator, a plurality of hollow fibers are prepared and each hollow fiber is coated at its ends with a fine resin powder. The coated ends of each fiber are heated so that the fibers are fixed one by one so as to form a fiber bundle. The

thus obtained fiber bundle is set in a housing together with a fine resin powder and a sheet such that the fibers are mechanically clamped. Then, heat is applied so as to weld the fiber bundle to the housing.

In another preferred form of the method of the invention, a housing is disassembled to halves to each of which a bundle of fibers is welded and then the halves of the housing are assembled together to complete the module. Alternatively, a fiber bundle is formed by arraying a plurality of hollow fibers in a side-by-side fashion with the ends of the fibers coated with a fine resin powder. The coated ends of the fibers are sandwiched between sheets of the same resin as the fine powder and pressure and heat are applied to the sheets so that the fibers are hermetically welded at their ends to each other and to the sheets, whereby an assembly resembling a reed-screen is prepared. This assembly is then rolled and set in a housing and then heat and pressure are applied to the ends of the fiber bundle so as to weld the fibers again so as to provide seals between both sheets and the sheets and the housing.

Although the invention does not pose any restriction on the form of the module, the hollow-fiber type module is preferred because it can withstand higher filtration pressure as compared with other types of module such as pleats-type module, spiral-type module and tubular-type module. In addition, this type of module provides a greater effective area per unit volume so that the size and cost can be reduced economically. For these reasons, the hollow-fiber type module can be used in various fields and, hence, is preferred. From the view point of easiness of handling and use, the module is preferably constructed such that the fiber bundle is arranged straight and sealed at its both ends or such that the bundle is bent in a U-shaped form and sealed at both ends at one side of the module.

Fig. 22 shows the appearance of a hollow fiber module as an embodiment of the separator in accordance with the present invention, while Fig. 23 is a cross-sectional view of the element shown in Fig. 22.

The hollow fiber module according to the present invention has a plurality of hollow fibers 3 covered by a protective cover 4 arranged in the form of a bundle, the ends of the hollow fibers 3 being fixed through welding with a housing seal member 5 and a fixing resin 6.

The porous membrane module according to the present invention finds a wide use. More specifically, the porous module can be used in the following fields: production of a highly purified water or chemicals of high degrees of purity used in semiconductor industries; collection of effluents from defatting process or electrodeposition pro-

cess; treatment of waste liquids in various industrial processes such as paper-making process, oil-water separation process, oily emulsion separation process, and so forth; separation and refining of fermented products; condensation, separation and refining in various food industries such as condensation of fruit and vegetable juices, processing of soybean, production of sugar, and so forth; medical uses such as artificial kidney, micro-filter for separation of blood components and bacterium, and separator or refiner for medical drugs; bio-technological devices such as a bio-reactor; electrodes of a fuel battery; and so forth.

The separator making use of the porous membrane of the present invention features an extremely small rate of elution, as well as excellent heat- and chemical-resistances, thanks to the use of the PTFE resin as the material of the porous membrane and the porous membrane module. In addition, a porous membrane having a reduced thickness can be produced without difficulty. Moreover, a separation membrane having a variety of pore size distribution can be obtained by adding an additive or by changing the composition of the mixture. In the production of the separator, the process for forming the porous membrane can be incorporated in the process for forming a separator module. Although some examples are shown below, it is to be noted that they are only illustrative and are not intended for limiting the scope of the invention.

Factors employed in the following description of Examples were respectively measured in accordance with the following methods:

(1) Dimensions of membrane

Dimensions of the membrane were measured by observation through an optical microscope.

(2) Size of pores in membrane

The pore size was measured by photographic observation through a scanning electronic microscope (Model α -9, produced by Akashi Seisakusho).

(3) Porosity

The porosity was calculated in accordance with the following formula:

$$(W - W_0) \times 100/V \quad (\%)$$

where, W represents the weight of the membrane as measured when the pores were filled with purified water by ethanol substitution method, W_0 re-

presents the absolute dry weight of the membrane, and V represents the volume of the membrane.

(4) Water permeability

In case of a sheet-type membrane, the membrane was incorporated in a commercially available cartridge and a hydrostatic pressure was applied to the membrane while the membrane was maintained at 37°C. The water permeability was then calculated from the amount of water permeating through the membrane in a given time, effective membrane area and the pressure differential across the membrane.

In case of a hollow fiber type module, the fibers were assembled to form a compact module and a hydrostatic pressure was applied to the interior of the fibers while the fibers were maintained at 37°C. The water permeability was calculated from the amount of water which has permeated through the membrane, effective area of the membrane and the pressure differential across the membrane.

(5) Filtration performance on 5% aqueous solution of albumin

Water permeability was measured by the same method as (3) described above, by making use of a commercially available cow blood serum (Fraction V). Then, the albumin blocking rate was calculated in accordance with the following formula:

$$(C_0 - C) \times 100/C_0 \quad (\%)$$

where, C_0 represents the concentration of the original liquid, while C represents the concentration of the liquid permeated through the membrane.

Example 1

50 parts of sodium alginate (Produced by Nakai Kagakusha, 300 cps) was dissolved in 950 parts of refined water at 70°C so as to form a uniform liquid. Then, 200 parts of aqueous dispersion of PTFE (D-2 produced by Daikin: solid content 61 wt%, surfactant 5.7 wt%) and 13 parts of a silicone oil (SH-200 produced by Toray Silicone) were added to the above-mentioned liquid. The liquid was then stirred at 70°C so that a uniform original liquid was prepared. This original liquid had a viscosity of about 290 poise at 40°C. The original liquid was then spread on a glass sheet at 40°C and, immediately thereafter, immersed in 40 wt% of aqueous solution of calcium chloride heated to 40°C for 5 minutes. The liquid glass sheet was then dipped in water of the room temperature.

whereby a flat-sheet type membrane was formed. The thus obtained sheet was heated in a hot-air oven and heat-treated for 30 minutes at 340°C. Then, the membrane was kept whole through a night in a mixture of the room temperature containing about 70 wt% of sulfuric acid and about 30 wt% of nitric acid so as to remove the sodium alginate, silicone oil and denaturation product formed therefrom as a result of the heat-treatment. The membrane was then rinsed with water, whereby a porous membrane was obtained. The structure of this membrane is shown in Figs. 1, 2 and 3. As will be seen from these Figures, the membrane had three-dimensional reticulated or network structure with multiplicity of pores of 0.5 to 1.0μ in and under the surfaces thereof.

This membrane had a porosity of about 20% and a thickness of about 110μ in wetted condition. The permeability to purified water was 310 ml/m²·hr·mmHg, while the permeation performance test conducted with 5% albumin aqueous solution showed a water-permeability of 24ml/m²·hr·mmHg and an albumin blocking rate of 66%.

Example 2

The original liquid used in Example 1 was extruded through a hollow-fiber spinneret of 40°C together with a core liquid which was about 10 wt% aqueous solution of calcium chloride. The extruded liquid was made to run 5cm through the air and was introduced into a coagulating bath of about 50°C consisting of about 40 wt% aqueous solution of calcium chloride so as to be coagulated. The fiber thus formed by coagulation was rinsed with water and was wound up at a speed of 20 m/min. The thus formed fiber was heated at 340°C for 30 minutes in a hot air oven and was then kept whole through a night in a mixture liquid of the room temperature containing about 70 wt% of sulfuric acid and about 30 wt% of nitric acid, so as to remove the sodium alginate and silicone oil, as well as the denaturation products formed therefrom as a result of the heat-treatment. The fiber was then rinsed with water to wash away any residue, whereby a porous membrane of hollow fiber was obtained. The structure of this membrane is shown in Figs. 4, 5 and 6. As will be seen from these Figures, the membrane had a three-dimensional reticulated or network structure with pores of 0.5 to 1.0μ in and under the surfaces thereof.

This membrane had a porosity of about 22%, as well as an inside diameter of about 360μ and a thickness of about 70μ in wetted condition. The permeability to purified water was 36 ml/m²·hr·mmHg, while the permeation perfor-

mance test conducted with 5% albumin aqueous solution showed a water-permeability of 7.4ml/m²·hr·mmHg and an albumin blocking rate of 66%.

Stainless steel filaments of 100 mm long were inserted to both open ends of the hollow fiber to a depth of about 50 mm. 400 pieces of such fibers were bent in a U-like form to form a bundle. The end of this bundle, 50 mm in length, was dipped for 15 seconds in an aqueous dispersion (D-2 produced by Daikin: solid content 61 wt% and surfactant content 5.7 wt%) of PTFE (melting point 327°C). The wetted end of the hollow fiber bundle was then dried at the room temperature so that a thin membrane of hollow resin was formed on the surfaces of the hollow fibers of the bundle. The dipping and drying were repeated five times in total so that a coating membrane of the resin was uniformly formed on the surfaces of the hollow fibers. The coated portion of the fiber bundle was then clamped with a jig of a stainless steel with the intermediary of PTFE films (melting point 327°C) and heat was applied only to the end of the fiber bundle in a concentrated manner by means of a heat gun, whereby the polymer was molten to fix the hollow fibers. Then, after removing the jig, a PTFE film (melting point 327°C) was wound on the welded portion of the hollow fiber bundle and a housing seal member of PTFE was fitted on the membrane. Heat was applied once again by the heat gun concentrically to the end of the fiber bundle, whereby the seal member was fixed to the fiber bundle.

Subsequently, the bundle of the hollow fibers was sliced at its end to which the seal member was fixed, so that an element was obtained in which the hollows of the fibers were opened. The thus obtained element was immersed in ethanol for 2 hours for the purpose of a hydrophilic treatment, followed by an air leak test. No leakage was observed at the sealed portion of the element. After the treatment for realizing the hydrophilic nature of the element, water permeability was measured by applying water pressure of 1 kg/cm² from the outer side of the fibers. A water permeability level of 38 ml/min was confirmed.

Example 3

400 pieces of heat-treated hollow fibers, prepared by the same manner as Example 2 through the 30minute heat-treatment at 340°C, were bundled in a U-like form. The end of the bundle, 50 mm in length, was kept whole through a night in a mixture liquid of room temperature containing about 70 wt% of sulfuric acid and about 30 wt% of nitric acid so as to remove the sodium alginate and

the silicone oil, as well as denaturation product of the sodium alginate and the silicone oil formed as a result of the heat-treatment. Then the bundle was rinsed with water and stainless steel filaments of 100 mm long were inserted into the hollows of the filaments to a depth of 50 mm. Then, the end of the fiber bundle, 50 mm in length, was gently dipped in an aqueous dispersion (D-2 produced by Daikin: solid content 61 wt% and surfactant content 5.7 wt%) of PTFE (melting point 327°C) and kept therein for 15 seconds, followed by drying at the room temperature, whereby a thin membrane of the resin was formed on the surface of the hollow fiber bundle. The dipping and drying were repeated five times in total so that a coating membrane of the resin was uniformly formed on the surfaces of the hollow fibers. The coated portion of the fiber bundle was then clamped with a jig of a stainless steel with the intermediary of PTFE films (melting point 327°C). The hollow fiber bundle was then heated in an electric oven at 340°C so that the resin was molten to weld and fix the hollow fibers. Then, after removing the jig, a PTFE film (melting point 327°C) was wound on the welded portion of the hollow fiber bundle and a housing seal member of PTFE was fitted on the membrane. The bundle was then heated to 340°C in a vacuum atmosphere, whereby the seal member was fixed to the fiber bundle.

Subsequently, the the bundle of the hollow fibers was sliced at its end to which the seal member was fixed, so that an element was obtained in which the hollows of the fibers were opened. The thus obtained element was kept whole through a night in a room-temperature mixture liquid containing about 70 wt% of sulfuric acid and about 30 wt% of nitric acid, so as to remove the sodium alginate and the silicone oil, as well as the denaturation products thereof formed as a result of the heat-treatment. The element was then immersed in ethanol for 2 hours for the purpose of a hydrophilic treatment, followed by an air leak test. No leakage was observed at the sealed portion of the element. After the treatment for realizing the hydrophilic nature of the element, water permeability was measured by applying water pressure of 1 kg/cm² from the outer side of the fibers. A water permeability level of 38 ml/min was confirmed.

Example 4

The wetted porous hollow fiber membrane after the acid cleaning and water rinsing in Example 2 was drawn at a ratio of 1.5. The structure of the membrane is shown in Figs. 7, 8 and 9. As shown in these Figures, a fine structure layer with pores of 0.5 to 1.0μ in pore size was formed on the surface

of the membrane. The size of the pores in and under the surface of the membrane ranged between 0.3 and 2.0μ.

The porosity of the hollow fiber membrane was about 40%. The inside diameter and the thickness of the wetted hollow fiber membrane were about 330μ and about 67μ, respectively. The permeability to purified water was 259 ml/m²·hr·mmHg, while a permeability performance test conducted with 5% aqueous solution of albumin showed water permeability of 50ml/m²·hr·mmHg and an albumin blocking rate of about 38%.

Comparison Example 1

A flat sheet membrane and a hollow fiber membrane were prepared in the same manners as Examples 1 and 2, except that the heat-treating temperature was changed to 310°C. These membranes were kept whole through a night in a room-temperature mixture liquid containing about 70 wt% of sulfuric acid and about 30 wt% of nitric acid so as to remove the sodium alginate and the silicone oil, as well as denaturation products thereof formed as a result of the heat-treatment. After the removal of these substances, the membranes could not support themselves and were collapsed.

Example 5

400 pieces of the porous hollow fibers after the acid cleaning and water rinsing in Example 2 were bundled and bent in a U-like form. The end of this bundle, 50 mm in length, was gently dipped for 15 seconds in an aqueous dispersion (solid content 50 wt%, viscosity 20 cp, specific gravity 1.4) of a tetrafluoroethylene-hexafluoropropylene copolymer (melting point 270°C), followed by drying at the room temperature so that a thin membrane of the resin was formed on the surfaces of the hollow fibers. The dipping and drying were repeated 5 times so that a coating membrane of the resin was uniformly formed on the surface of the hollow fibers. Subsequently, the portion of the fiber bundle coated with this coating membrane was clamped with a stainless steel jig through the intermediary of films of the tetrafluoroethylene-hexafluoropropylene copolymer (melting point 270°C) and the bundle thus clamped was heated in an electric oven at 320°C, whereby the resin was molten to weld the hollow fibers without inclusion of any continuous void. After removal of the jig, a housing seal member of PTFE was fitted on the welded portion of the hollow fibers, with gaps filled with pellets of the tetrafluoroethylene-hexafluoropropylene copolymer (melting point 270°C). The bundle was then heated

at 320° C in a vacuum atmosphere so that the seal member was fixed to the bundle of hollow fibers. The bundle was then sliced at its portion covered by the seal member, whereby an element with hollows of fibers opened was obtained. This element was immersed in ethanol for 2 hours for the purpose of hydrophilic treatment, followed by an air leak test which showed no leakage at the seal portion.

Example 6

Dipping treatment was conducted in the same manner as Example 5 except that an aqueous dispersion (solid content 50 wt%, viscosity 250 cp, specific gravity 1.4) of tetrafluoroethylene-perfluoroalkylvinyl copolymer (melting point 310° C) was used. The bundle of hollow fibers, coated by a uniform resin coating membrane, was fixed to the center of a housing seal member, and the gaps between adjacent hollow fibers, as well as the gaps between the hollow fibers and the seal member, were filled with a powder of tetrafluoroethylene-perfluoroalkylvinyl copolymer (melting point 310° C) with the aid of a vibrator. The hollow fiber bundle was then placed in a vacuum container of a stainless steel so as to be heated at 320° C in a vacuum atmosphere, whereby the resin was molten to weld the end of the hollow fiber bundle to the housing seal member. Then, by slicing the portion of the bundle fixed to the seal member, an element with the hollows of fibers opened was obtained. The thus obtained element was immersed for 2 hours in ethanol for hydrophilic treatment followed by an air leak test in which no leakage was recognized.

Example 7

A uniform mixture liquid was prepared by dissolving, in 950 parts of refined water, 50 parts of sodium alginate (produced by Nakai Kagaku-sha, 300 cps), 20 parts of calcium carbonate (produced by Nakai Kagaku-sha, special grade reagent) and 12 parts of silicone oil (SH-200 produced by Toray Silicone), and blending them at 70° C. Then, 200 parts of an aqueous PTFE dispersion (D-2 produced by Daikin: solid content 61 wt%, surfactant content 5.7 wt%) was added to the above-mentioned mixture liquid and the mixture was stirred at 70° C whereby a uniform original liquid was obtained. This original liquid showed a viscosity of about 420 poise at 40° C. The original liquid was spread on a glass sheet and was dipped without delay in a 40 wt% aqueous solution of calcium chloride heated to 40° C and kept in this solution

for 5 minutes. The glass sheet was then dipped in water of the room temperature, whereby a flat sheet-like membrane was formed. The membrane was then heat-treated at 340° C for 30 minutes in a hot-air oven and was then kept whole through a night in a room-temperature mixture liquid containing about 70 wt% of sulfuric acid and about 30 wt% of nitric acid so as to remove the sodium alginate, the silicone oil, denaturation products thereof formed as a result of the heat treatment, and the calcium carbonate. Then, the membrane was rinsed with water to become a porous membrane. Figs. 10, 11 and 12 show the structure of the thus obtained porous membrane. As will be understood from these Figures, the membrane had a fine structure layer with a surface 1a contacted the coagulation liquid and having pores of a mean pore size of 0.5 μ and a thickness of 3 μ , another fine structure layer with a surface 1b contacted the glass sheet and having pores of a mean pore size of 0.3 μ and a thickness of 3 μ , and an intermediate support layer having pores of 3 to 15 μ and a thickness of 190 μ .

The membrane had a porosity of about 60%, while the thickness of this membrane in wetted state was about 200 μ . The permeability to purified water was 5800 ml/m²·hr·mmHg. A permeability performance test conducted with a 5% aqueous solution of albumin showed a water-permeability of 480 ml/m²·hr·mmHg and an albumin blocking rate of about 3%.

Example 8

The original liquid used in Example 7 was extruded through a hollow-fiber spinneret of 40° C together with a core liquid which was about 10 wt% aqueous solution of calcium chloride. The extruded liquid was made to run 5cm through the air and was introduced into a coagulating bath of about 50° C consisting of about 40 wt% aqueous solution of calcium chloride so as to be coagulated. The fiber thus formed by coagulation was rinsed with water and was wound up at a speed of 20 m/min. The thus formed fiber was heat-treated at 340° C for 30 minutes in a hot air oven and was then kept whole through a night in a mixture liquid of the room temperature containing about 70 wt% of sulfuric acid and about 30 wt% of nitric acid, so as to remove the sodium alginate, the silicone oil, the denaturation products formed therefrom as a result of the heat-treatment, and the calcium carbonate. The fiber was then rinsed with water to wash away any residue, whereby a porous membrane of hollow fiber was obtained. The structure of this membrane is shown in Figs. 13, 14 and 15. As will be seen from these Figures, the membrane had a fine

structure layer providing an outer surface 1a of the membrane and having pores of a mean pore size of 0.5μ and a thickness of about 2μ , another fine structure layer presenting the inner surface 1b and having a mean pore size of 0.8μ and a thickness of about 2μ , and an intermediate support layer having a multiplicity of pores of 1 to 15μ and a thickness of about 90μ .

This hollow fiber membrane had a porosity of about 50%, as well as an inside diameter of about 360μ and a thickness of about 95μ in wetted condition. The permeability to purified water was $450 \text{ ml/m}^2 \cdot \text{hr} \cdot \text{mmHg}$, while the permeation performance test conducted with 5% albumin aqueous solution showed a water-permeability of $90 \text{ ml/m}^2 \cdot \text{hr} \cdot \text{mmHg}$ and an albumin blocking rate of about 2%.

Comparison Example 2

A flat sheet membrane and a hollow fiber membrane were prepared in the same manners as Examples 7 and 8, except that the heat-treating temperature was changed to 310°C . These membranes were kept whole through a night in a room-temperature mixture liquid containing about 70 wt% of sulfuric acid and about 30 wt% of nitric acid so as to remove the sodium alginate, the silicone oil, the denaturation products thereof formed as a result of the heat-treatment and the calcium carbonate. After the removal of these substances, the membranes could not support themselves and were collapsed.

Example 9

A uniform mixture liquid was prepared by dissolving, in 950 parts of refined water, 50 parts of sodium alginate (produced by Nakai Kagaku-sha, 300 cps), 250 parts of barium sulfate (X-ray contrast media Baritop, produced by Sakai Kagaku Kogyo) and 12 parts of silicone oil (SH-200 produced by Toray Silicone), and blending them at 35°C . Then, 200 parts of an aqueous PTFE dispersion (D-2 produced by Daikin: solid content 61 wt%, surfactant content 5.7 wt%) was added to the above-mentioned mixture liquid and the mixture was stirred at 35°C whereby a uniform original liquid was obtained. This original liquid showed a viscosity of about 420 poise at 30°C . The original liquid was spread on a glass sheet and was dipped without delay in a 40 wt% aqueous solution of calcium chloride heated to 40°C and kept in this solution for 5 minutes. The glass sheet was then dipped in water of the room temperature, whereby a flat sheet-like membrane was formed. The mem-

brane was then heat-treated at 340°C for 30 minutes in a hot-air oven and was then kept whole through a night in a room-temperature mixture liquid containing about 70 wt% of sulfuric acid and about 30 wt% of nitric acid so as to remove the sodium alginate, the silicone oil, denaturation products thereof formed as a result of the heat treatment, and the barium sulfate. Then, the membrane was rinsed with water and bi-axially drawn at a ratio of 1.5 to become a porous membrane. Figs. 16, 17 and 18 show the structure of the thus obtained porous membrane. As will be understood from these Figures, the membrane had a fine structure layer with a surface 1 contacted the coagulation liquid and having pores of a mean pore size of 0.6μ and a thickness of about 2μ , and a support layer having pores of 1 to 6μ and a thickness of 108μ .

The membrane had a porosity of about 60%, while the thickness of this membrane in wetted state was about 110μ . The permeability to purified water was $11800 \text{ ml/m}^2 \cdot \text{hr} \cdot \text{mmHg}$. A permeability performance test conducted with a 5% aqueous solution of albumin showed a water-permeability of $140 \text{ ml/m}^2 \cdot \text{hr} \cdot \text{mmHg}$ and an albumin blocking rate of about 44%.

Example 10

The original liquid used in Example 9 was extruded through a hollow-fiber spinneret of 30°C together with a core liquid which was about 10 wt% aqueous solution of calcium chloride. The extruded liquid was made to run 5cm through the air and was introduced into a coagulating bath of about 40°C consisting of about 40 wt% aqueous solution of calcium chloride so as to be coagulated. The fiber thus formed by coagulation was rinsed with water and was wound up at a speed of 20 m/min. The thus formed fiber was heat-treated at 340°C for 30 minutes in a hot air oven and was then kept whole through a night in a mixture liquid of the room temperature containing about 70 wt% of sulfuric acid and about 30 wt% of nitric acid, so as to remove the sodium alginate, the silicone oil, the denaturation products formed from the sodium alginate and the silicone oil as a result of the heat-treatment, and the barium sulfate. The fiber was then rinsed with water to wash away any residue and then drawn at a ratio of 1.5, whereby a porous membrane of hollow fiber was obtained. The structure of this membrane is shown in Figs. 19, 20 and 21. As will be seen from these Figures, the membrane had numerous fine pores of a mean pore size of 0.7μ .

This hollow fiber membrane had a porosity of about 50%, as well as an inside diameter of about

360 μ and a thickness of about 95 μ in wetted condition. The permeability to purified water was 1740 ml/m²·hr·mmHg, while the permeation performance test conducted with 5% albumin aqueous solution showed a water-permeability of 140ml/m²·hr·mmHg and an albumin blocking rate of about 51%.

Comparison Example 3

A flat sheet membrane and a hollow fiber membrane were prepared in the same manners as Examples 9 and 10, except that the heat-treating temperature was changed to 310 °C. These membranes were kept whole through a night in a room-temperature mixture liquid containing about 70 wt% of sulfuric acid and about 30 wt% of nitric acid so as to remove the sodium alginate, the silicone oil, the denaturation products thereof formed as a result of the heat-treatment, and the barium sulfate. After the removal of these substances, the membranes could not support themselves and were collapsed.

Brief Description of the Drawings

Fig. 1 shows a scanning electronic microscopic photograph (magnification 1600) of the surface of a porous membrane of Example 1 which has been kept in contact with a glass sheet;

Fig. 2 shows a scanning electronic microscopic photograph (magnification 560) of the structure exhibited by a sectional surface of the porous membrane of Example 1;

Fig. 3 shows a scanning electronic microscopic photograph (magnification 1600) of the surface of a porous membrane of Example 1 which has been kept in direct contact with a coagulation liquid;

Fig. 4 shows a scanning electronic microscopic photograph (magnification 4000) of the structure of the outer surface of a porous hollow fiber membrane of Example 2;

Fig. 5 shows a scanning electronic microscopic photograph (magnification 800) of the structure exhibited by a sectional surface of the porous hollow fiber membrane of Example 2;

Fig. 6 shows a scanning electronic microscopic photograph (magnification 1600) of the structure of the inner surface of the porous hollow fiber membrane of Example 2;

Fig. 7 shows a scanning electronic microscopic photograph (magnification 1600) of the structure of the outer surface of a porous hollow fiber membrane of Example 3;

Fig. 8 shows a scanning electronic microscopic photograph (magnification 800) of the structure exhibited by a sectional surface of the porous hollow fiber membrane of Example 3;

Fig. 9 shows a scanning electronic microscopic photograph (magnification 1600) of the structure of the inner surface of the porous hollow fiber membrane of Example 3;

Fig. 10 shows a scanning electronic microscopic photograph (magnification 2400) of the surface of a porous membrane of Example 7 which has been kept in direct contact with a coagulation liquid;

Fig. 11 shows a scanning electronic microscopic photograph (magnification 160) of the structure exhibited by a sectional surface of the porous membrane of Example 7;

Fig. 12 shows a scanning electronic microscopic photograph (magnification 2400) of the surface of the porous membrane of Example 7 which has been kept in contact with a glass sheet;

Fig. 13 shows a scanning electronic microscopic photograph (magnification 2400) of the structure of the outer surface of a porous hollow fiber membrane of Example 8;

Fig. 14 shows a scanning electronic microscopic photograph (magnification 560) of the structure exhibited by a sectional surface of the porous hollow fiber membrane of Example 8;

Fig. 15 shows a scanning electronic microscopic photograph (magnification 2400) of the structure of the inner surface of the porous hollow fiber membrane of Example 8, in which 1a and 1b denote fine structure layers and 2 denotes a support layer;

Fig. 16 shows a scanning electronic microscopic photograph (magnification 1600) of the surface of a porous membrane of Example 9 which has been kept in direct contact with a coagulation liquid;

Fig. 17 shows a scanning electronic microscopic photograph (magnification 560) of the structure exhibited by a sectional surface of the porous membrane of Example 9;

Fig. 18 shows a scanning electronic microscopic photograph (magnification 1600) of the surface of the porous membrane of Example 9 which has been kept in contact with a glass sheet;

Fig. 19 shows a scanning electronic microscopic photograph (magnification 4000) of the structure of the inner surface of the porous hollow fiber membrane of Example 10;

Fig. 20 shows a scanning electronic microscopic photograph (magnification 560) of the structure exhibited by a sectional surface of the porous hollow fiber membrane of Example 10;

Fig. 21 shows a scanning electronic microscopic photograph (magnification 4000) of the structure of the outer surface of a porous hollow fiber membrane of Example 10;

Fig. 22 shows an appearance of an example of a separator element of hollow fiber module type; and

Fig. 23 is a sectional view of an example of an element, in which 3 denotes hollow fibers, 4 denotes a protective cover, 5 denotes a housing seal member, and 6 denotes a fixing resin.

Claims

1. A porous hollow fiber membrane made from a material containing, as its main component, a polytetrafluoroethylene resin.

2. A porous hollow fiber membrane according to Claim 1, wherein the sizes of discrete pores range between 0.01 and 2 μ .

3. A porous hollow fiber membrane according to Claim 1, wherein said polytetrafluoroethylene resin is selected from a group consisting of a tetrafluoroethylene homopolymer, a tetrafluoroethylene-perfluoroalkylvinyl ether copolymer, a tetrafluoroethylene-hexafluoropropylene copolymer, a tetrafluoroethylene-ethylene copolymer, and a mixture of these polymers.

4. A porous hollow fiber membrane according to Claim 1, composed of a resin particle bond structure substantially devoid of fibrillated portion.

5. A method of producing a porous membrane comprising:
forming a membrane having a hollow construction or a sheet-like construction from a mixture of a polytetrafluoroethylene resin dispersion and a fiber-forming polymer;
heat-treating said membrane at a temperature not lower than the melting point of said resin; and
removing said fiber-forming polymer.

6. A method of producing a porous membrane according to Claim 1, wherein said polytetrafluoroethylene resin is selected from a group consisting of a tetrafluoroethylene homopolymer, a tetrafluoroethylene-perfluoroalkylvinylet copolymer, a tetrafluoroethylene-hexafluoropropylene copolymer, a tetrafluoroethylene-ethylene copolymer, and a mixture of these polymers.

7. A method of producing a porous membrane according to Claim 5, wherein said polytetrafluoroethylene resin dispersion is an aqueous dispersion.

8. A method of producing a porous membrane according to Claim 5, wherein the size of the resin particles in said polytetrafluoroethylene resin dispersion is not greater than 1 μ .

9. A method of producing a porous membrane according to Claim 5, wherein said fiber-forming polymer is selected from a group consisting of a polyvinyl alcohol, a sodium alginate and a mixture thereof.

10. A method of producing a porous membrane comprising:

forming a membrane having a hollow construction or a sheet-like construction from a mixture of a polytetrafluoroethylene resin dispersion, a finely dispersible additive other than said resin, and a fiber-forming polymer;
heat-treating said membrane at a temperature not lower than the melting point of said resin; and
removing said fiber-forming polymer.

11. A method of producing a porous membrane according to Claim 5, wherein said finely dispersible additive is selected from a group consisting of inorganic particles, fine resin particles, heat-resistant organic matters and their mixtures.

12. A membrane-type separator comprising: a separator case; a porous membrane made mainly from a polytetrafluoroethylene resin; and a sealing material with which an end of said separator case is sealed, said sealing material containing a fluoro-resin.

13. A membrane-type separator according to Claim 12, wherein said porous membrane is a hollow fiber membrane.

14. A membrane-type separator according to Claim 12, wherein said fluoro-resin of said sealing material is selected from a group consisting of a polytetrafluoroethylene resin, tetrafluoroethylene-perfluoroalkylvinyl ether copolymer resin, a tetrafluoroethylene-hexafluoropropylene copolymer resin, a tetrafluoroethylene-ethylene copolymer resin, a chlorotrifluoroethylene polymer resin, a vinylidene fluoride polymer resin and a mixture thereof.

15. A membrane-type separator according to Claim 12, wherein said fluoro-resin of said sealing material is a polytetrafluoroethylene resin.

16. A method of producing a separator comprising:

forming a membrane having a hollow construction or a sheet-like construction from a mixture of a polytetrafluoroethylene resin dispersion and a fiber-forming polymer;
heat-treating said membrane at a temperature not lower than the melting point of said resin; and
effecting the following steps (1) and (2) in combination on the heat-treated film:

(1) removing said fiber-forming polymer, and
(2) mounting said membrane in a case so as to

form independent flow channels in said case and welding and fixing an end of said case with a fluoro-resin.

5

10

15

20

25

30

35

40

45

50

55

14

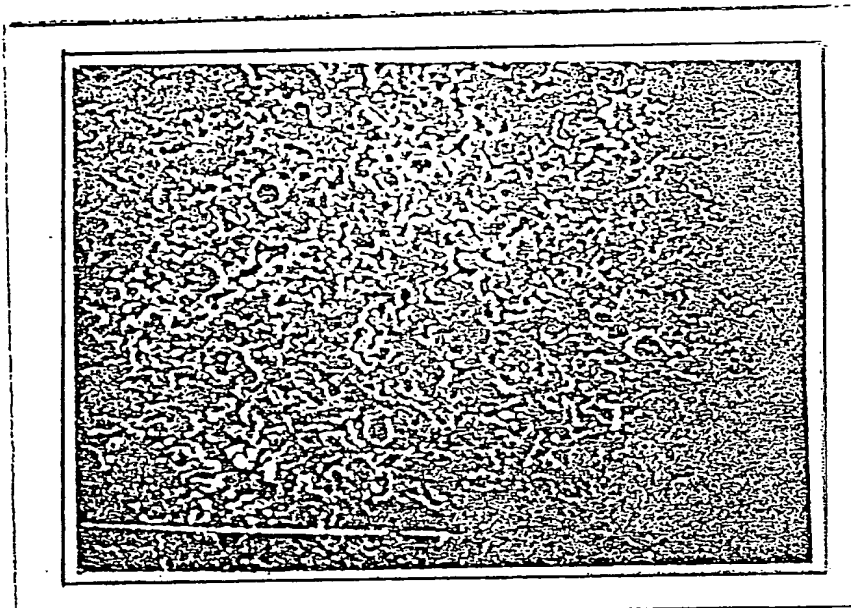


Fig. 1

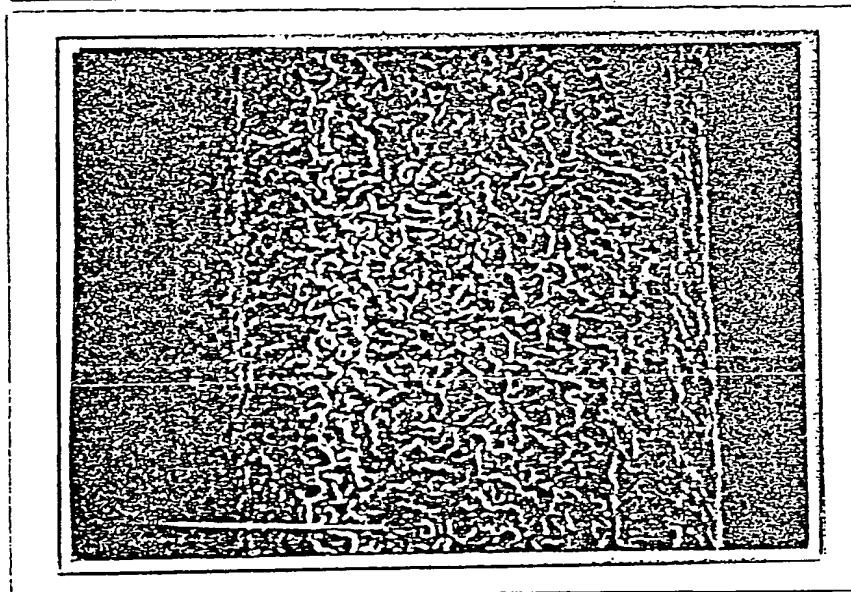


Fig. 2

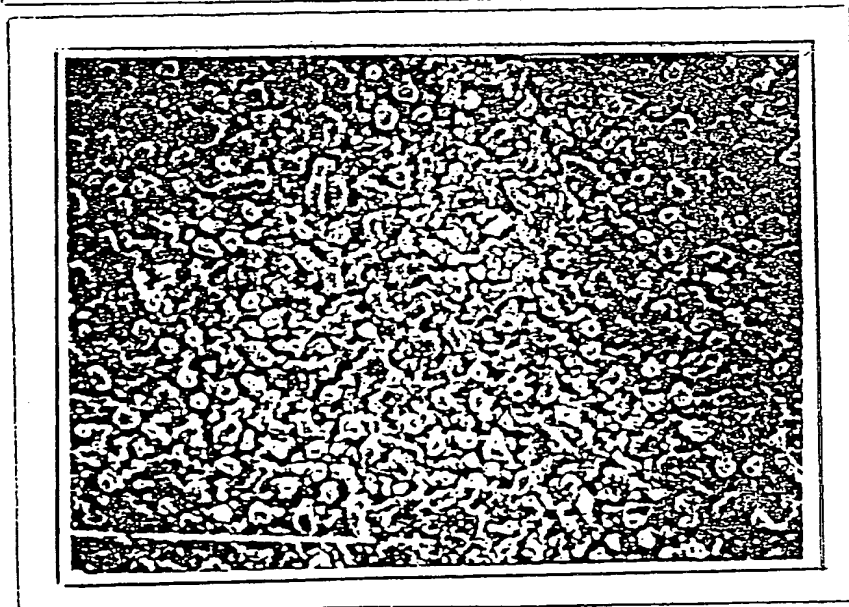


Fig. 3

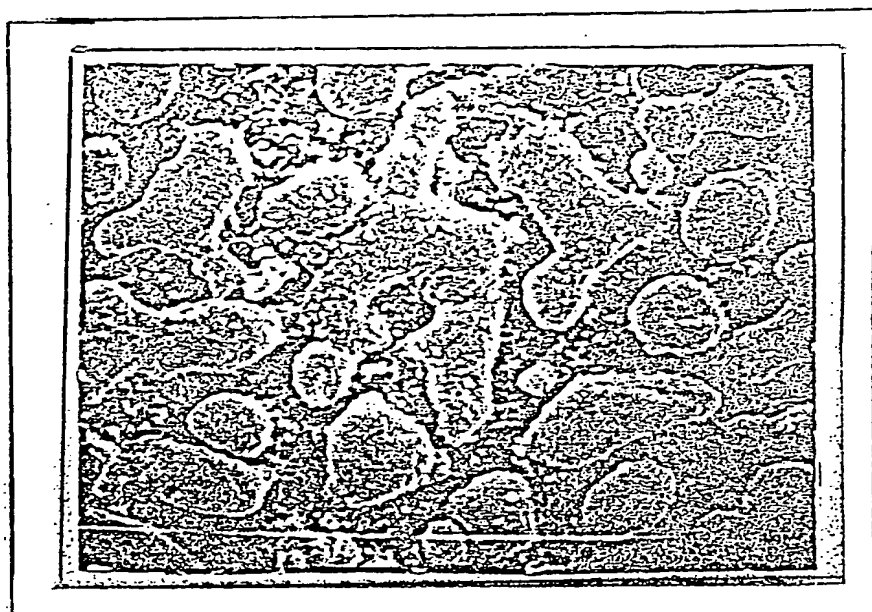


Fig. 4

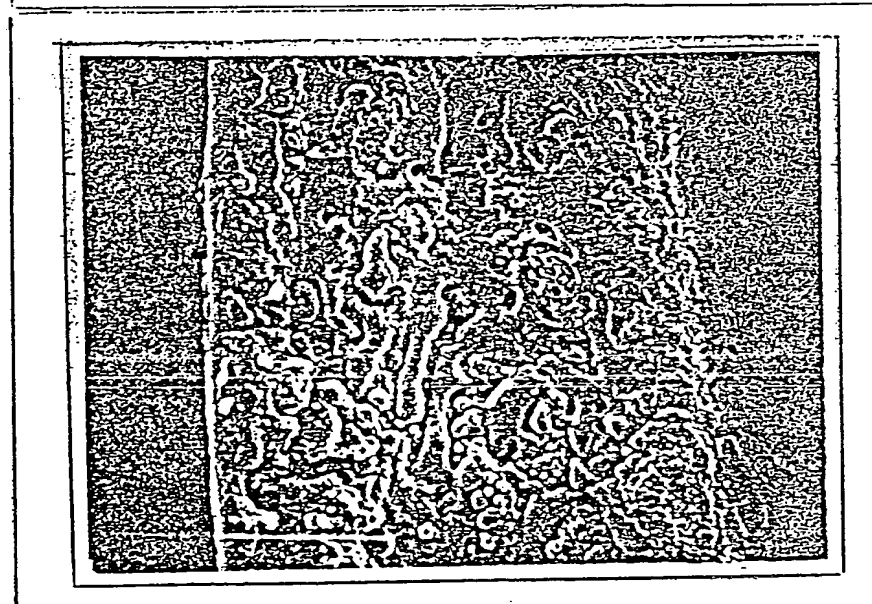


Fig. 5

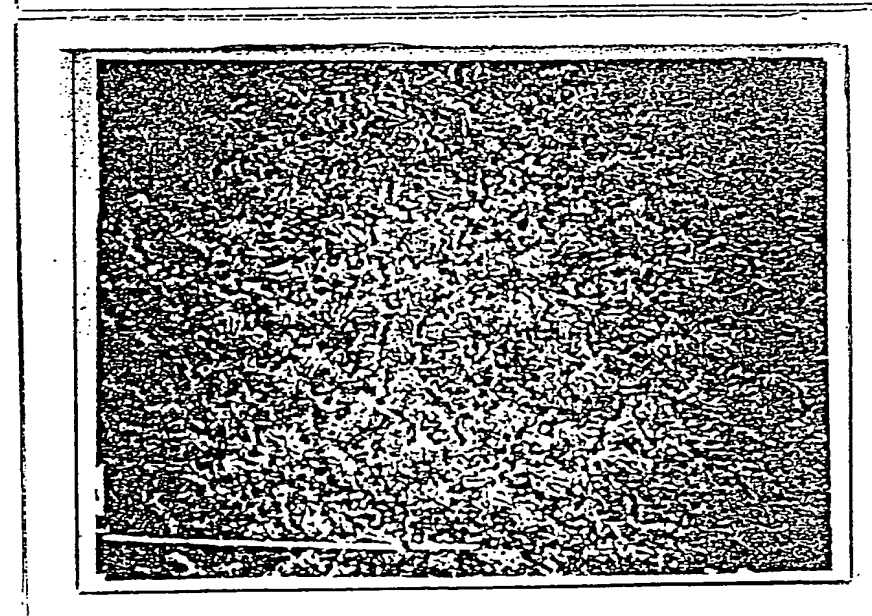


Fig. 6

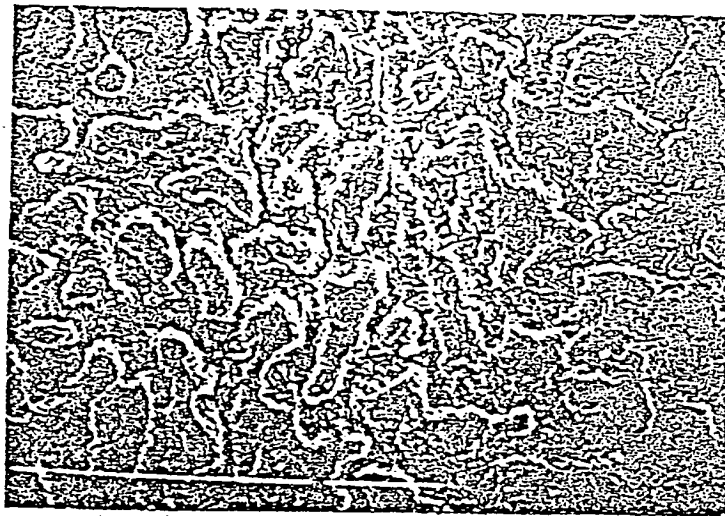


Fig. 7

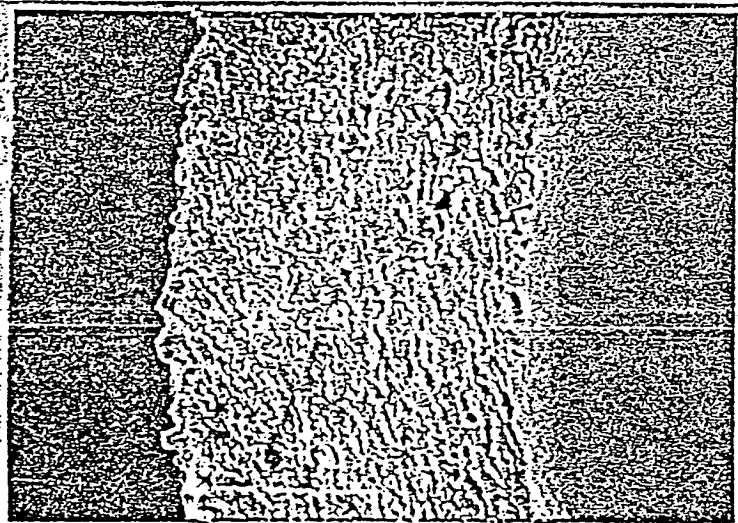


Fig. 8.

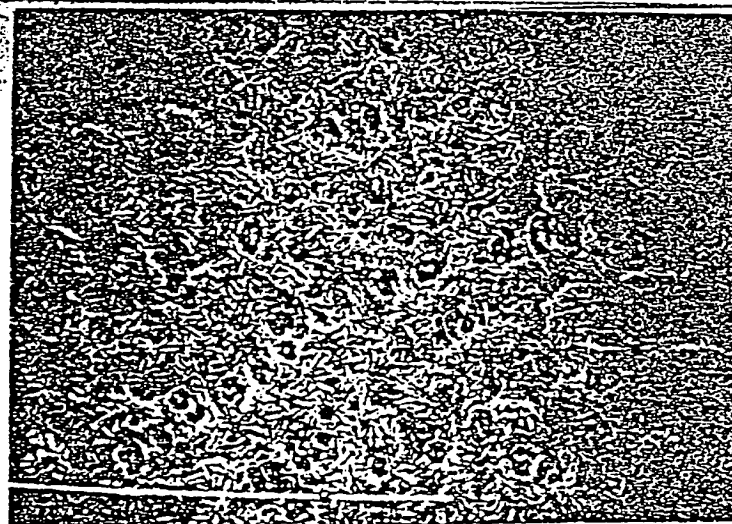


Fig. 9

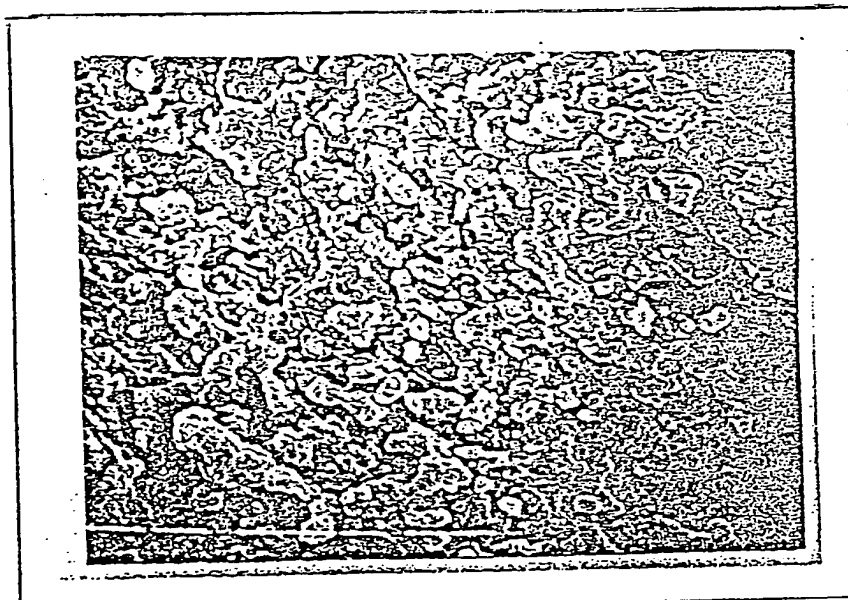


Fig. 10

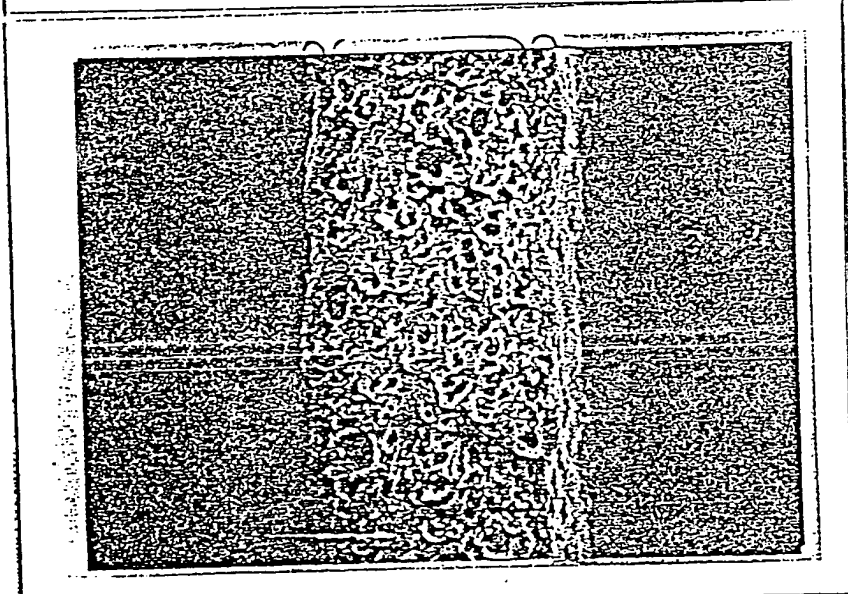


Fig. 11

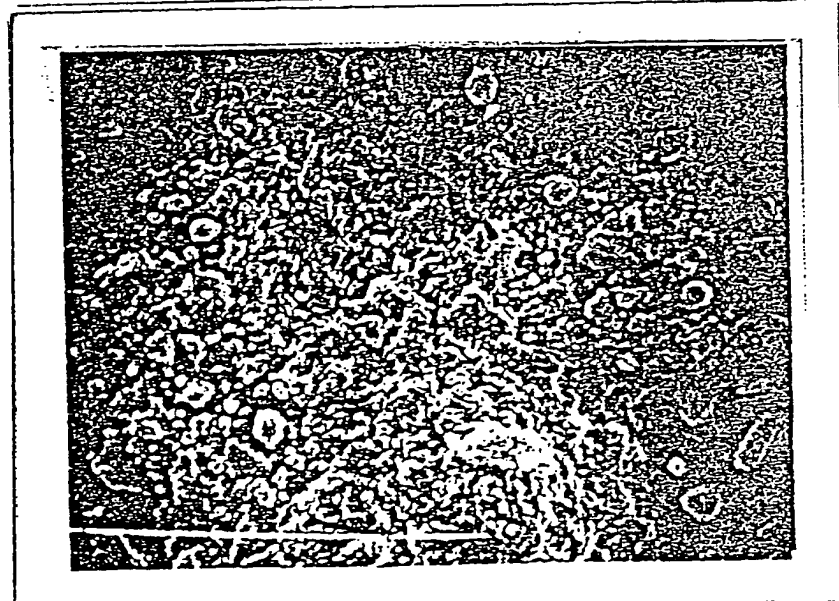


Fig. 12

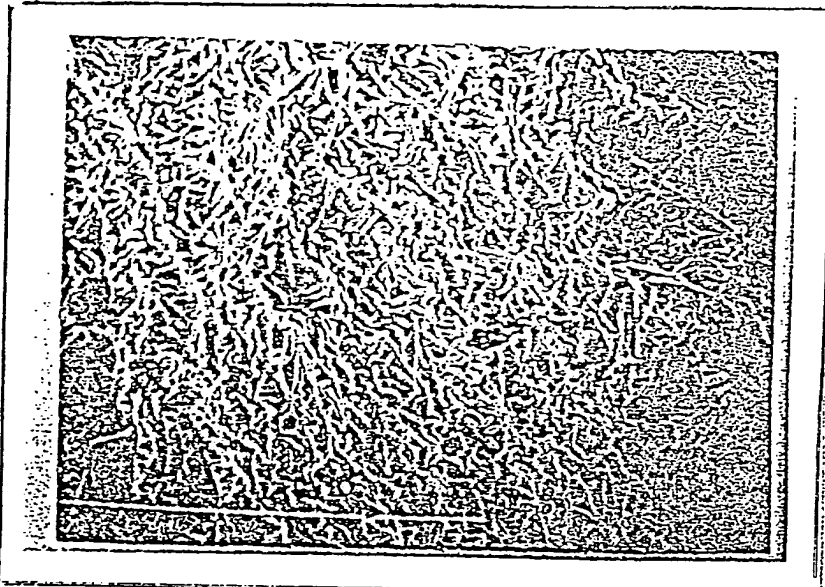


Fig. 13

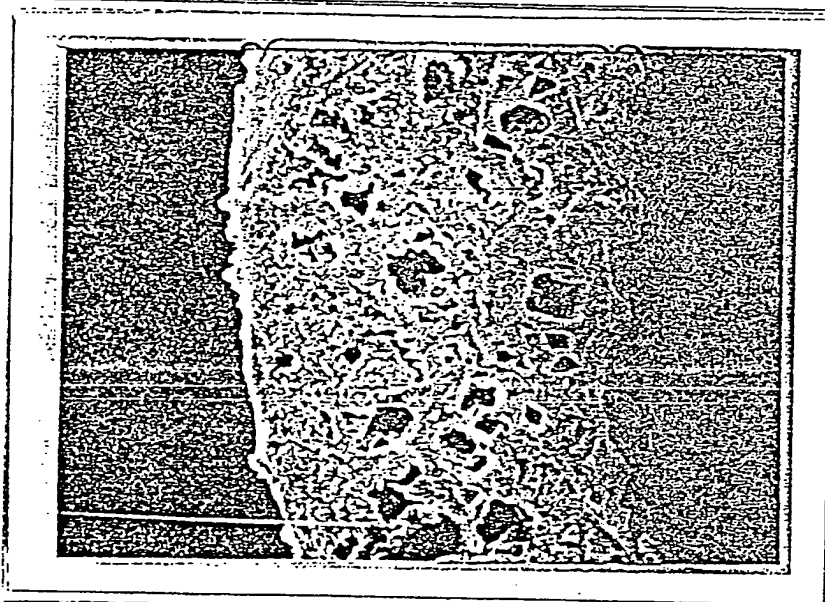


Fig. 14

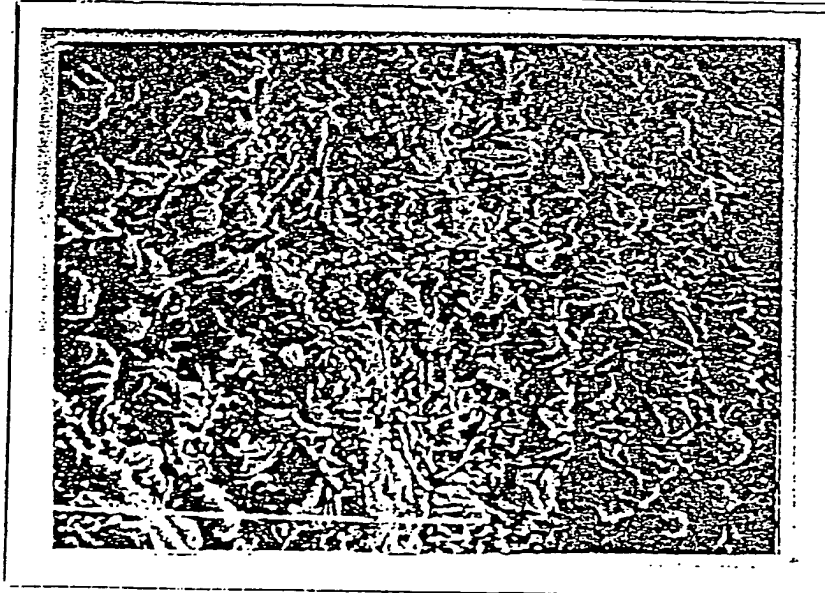


Fig. 15

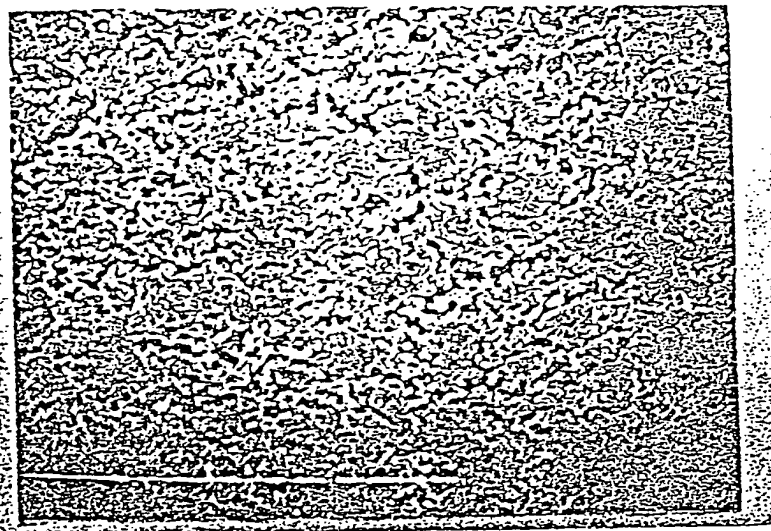


Fig. 16

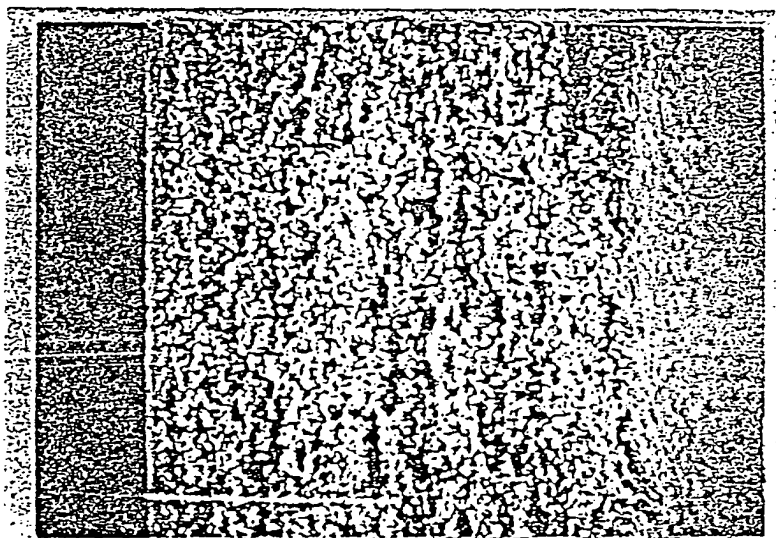


Fig. 17

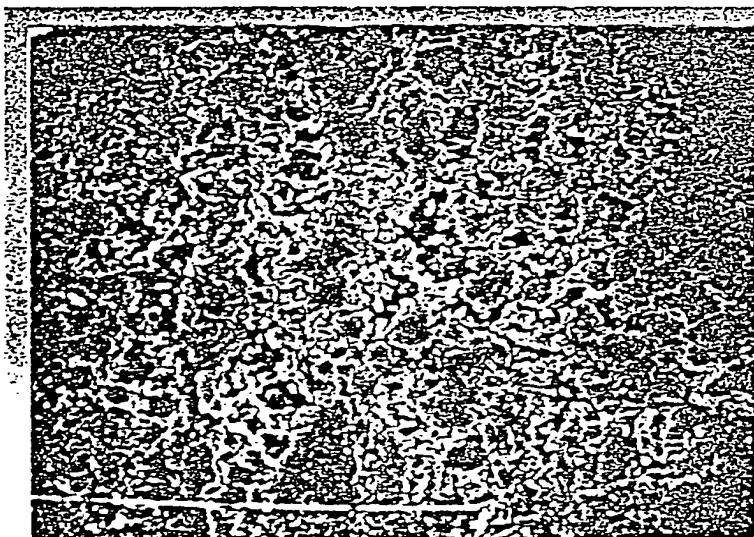


Fig. 18

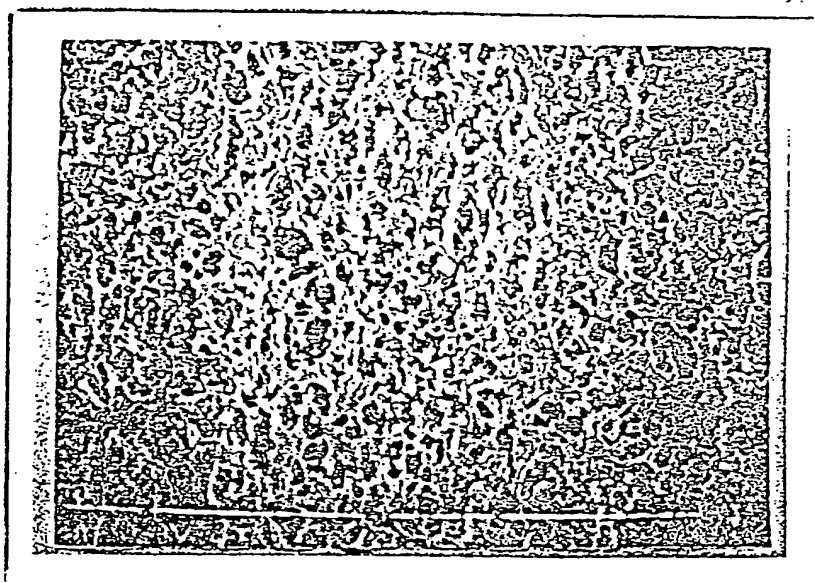


Fig. 19

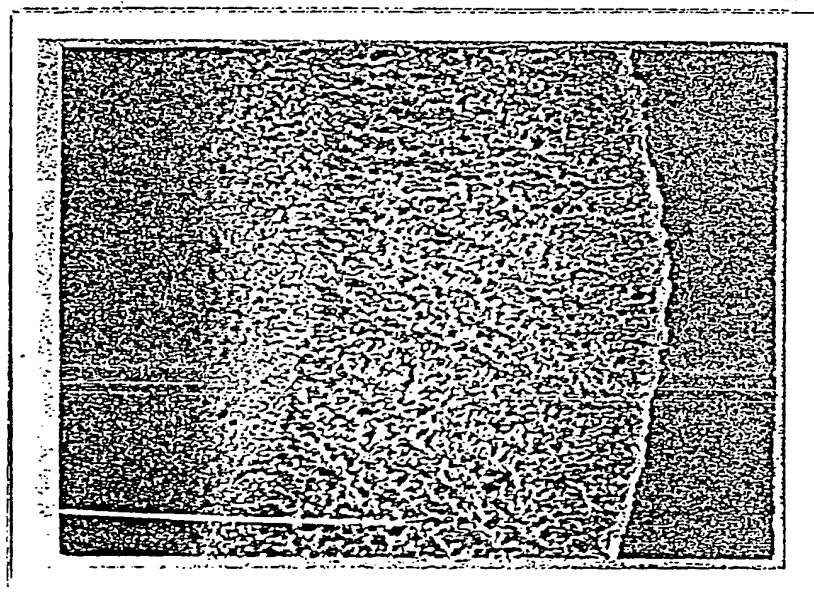


Fig. 20

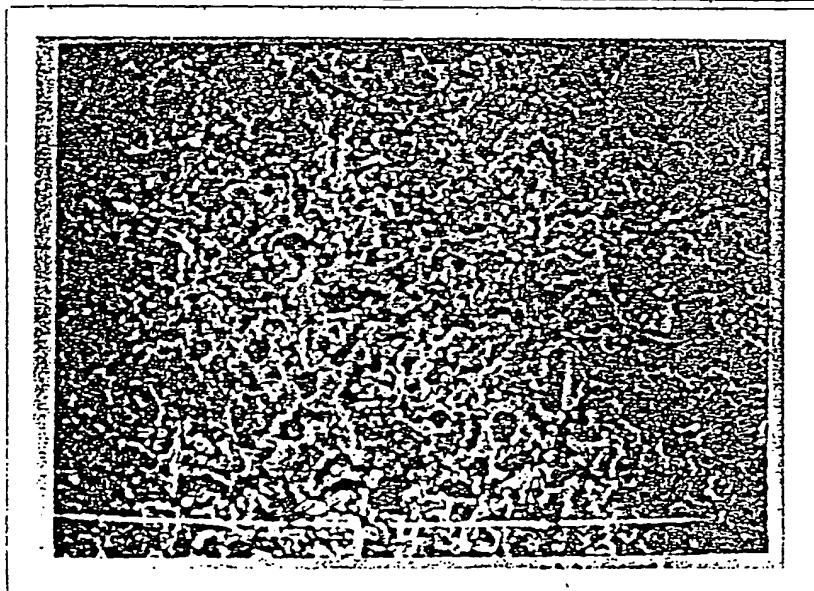


Fig. 21

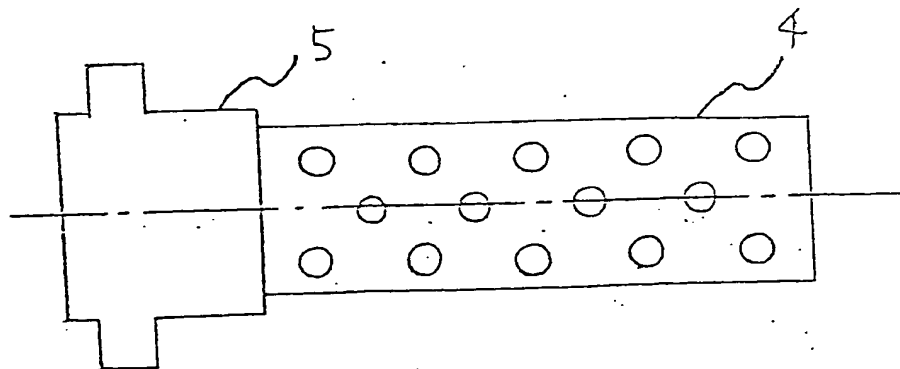


Fig. 22

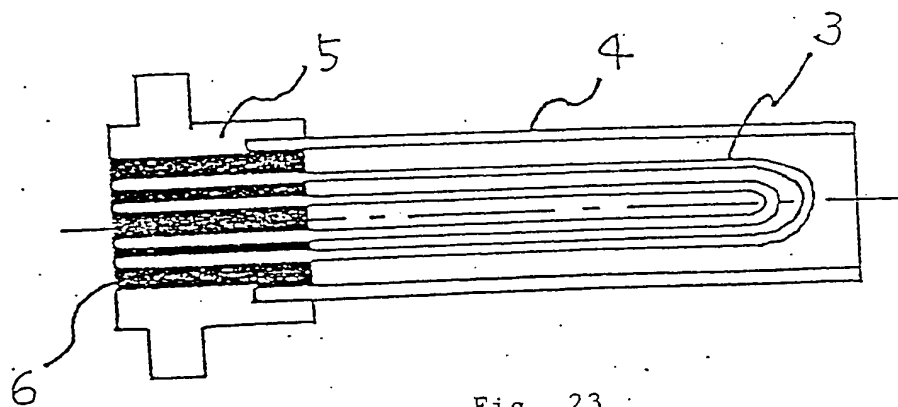


Fig. 23

INTERNATIONAL SEARCH REPORT

International Application

PCT/JP88/00755

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.C14 B01D13/01, B01D13/04, C08J9/26,
D01F6/12

II. FIELDS SEARCHED

Minimum Documentation Searched ⁷Classification System ¹

Classification Symbols

IPC

B01D13/01, B01D13/04, C08J9/26,
D01F6/12

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched ⁸

Jitsuyo Shinan Koho
Kokai jitsuyo Shinan Koho

1926 - 1988
1971 - 1988

III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹

| Category [*] | Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹² | Relevant to Claim No. ¹³ |
|-----------------------|--|-------------------------------------|
| X | JP, A, 60-53153 (Sumitomo Electric Industries, Ltd.) 26 March 1985 (26. 03. 85) Pages 1, 4 to 5 (Family: none) | 1, 3, 4 |
| X | JP, A, 59-5037 (Kogyo Gijutsuin-cho) 11 January 1984 (11. 01. 84) Page 4, lower part (Family: none) | 1-4 |
| Y | JP, A, 60-53153 (Sumitomo Electric Industries, Ltd.) 26 March 1985 (26. 03. 85) Pages 1, 4 to 5 (Family: none) | 5-11 |
| Y | JP, A, 59-5037 (Kogyo Gijutsuin-cho) 11 January 1984 (11. 01. 84) Page 4, lower part (Family: none) | 5-11 |
| Y | JP, A, 48-20780 (Yuasa Battery Co., Ltd.) 15 March 1973 (15. 03. 73) (Family: none) | 5-11 |

^{*} Special categories of cited documents: ¹⁰

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"Z" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

October 11, 1988 (11. 10. 88)

Date of Mailing of this International Search Report

October 24, 1988 (24. 10. 88)

International Searching Authority

Japanese Patent Office

Signature of Authorized Officer

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

| | | |
|---|--|-------|
| Y | JP, B1, 42-3691 (Toyo Rayon Kabushiki Kaisha) 16 February 1967 (16. 02. 67) (Family: none) | 5-11 |
| Y | JP, A, 60-53153 (Sumitomo Electric Industries, Ltd.) 26 March 1985 (26. 03. 85) Pages 1, 4 to 5 (Family: none) | 12-15 |
| Y | JP, A, 59-5037 (Kogyo Gijutsuin-cho) 11 January 1984 (11. 01. 84) Page 4, lower part (Family: none) | 12-15 |

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE¹⁰

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers because they relate to subject matter¹² not required to be searched by this Authority, namely:

2. ☐ Claim numbers because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out¹³, specifically:

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING¹⁴

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

- ☐ The additional search fees were accompanied by applicant's protest.
☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

| | | |
|---|--|-------|
| Y | JP, A, 61-129006 (Asahi Chemical Industry Co., Ltd.) 17 June 1986 (17. 06. 86) Pages 2 to 4 (Family: none) | 12-15 |
| Y | JP, A, 62-45302 (Asahi Chemical Industry Co., Ltd.) 27 February 1987 (27. 02. 87) (Family: none) | 12-15 |
| Y | JP, A, 60-53153 (Sumitomo Electric Industries, Ltd.) 26 March 1985 (26. 03. 85) | 16 |

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE¹⁰

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers because they relate to subject matter¹² not required to be searched by this Authority, namely:

2. ☐ Claim numbers because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out¹³, specifically:

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING¹¹

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

- ☐ The additional search fees were accompanied by applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

| | | |
|---|---|----|
| Y | Pages 1, 4 to 5 (Family: none) JP, A, 59-5037 (Kogyo Gijutsuin-cho) 11 January 1984 (11. 01. 84) Page 4, lower part (Family: none) | 16 |
| Y | JP, A, 61-129006 (Asahi Chemical Industry Co., Ltd.) 17 June 1986 (17. 06. 86) (Family: none) | 16 |
| Y | JP, A, 62-45302 (Asahi Chemical Industry Co., Ltd.) 27 February 1987 (27. 02. 87) (Family: none) | 16 |

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE¹⁰

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers..... because they relate to subject matter¹² not required to be searched by this Authority, namely:

2. ☐ Claim numbers..... because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out¹³, specifically:

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING¹¹

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:
3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims: it is covered by claim numbers:
4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

- ☐ The additional search fees were accompanied by applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUING FROM THE SECOND SHEET

| | | |
|---|---|----|
| Y | JP, A, 48-20780 (Yuasa Battery Co., Ltd.) 15 March 1973 (15. 03. 73) (Family: none) | 16 |
| Y | JP, B1, 42-3691 (Toyo Rayon Kabushiki Kaisha) 16 February 1967 (16. 02. 67) (Family: none) | 16 |

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE¹⁰

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers..... because they relate to subject matter¹² not required to be searched by this Authority, namely:

2. ☐ Claim numbers..... because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out¹³, specifically:

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING¹¹

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.



1
(

3

